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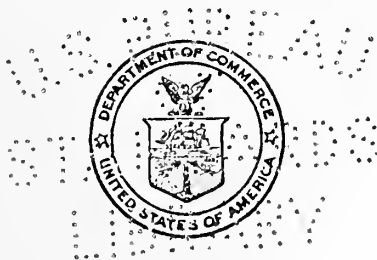
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OF THE

# BUREAU OF STANDARDS

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No. 432

[Part of Vol. 17]

## AN IMPROVED METHOD FOR PREPARING RAFFINOSE

BY

E. P. CLARK, Associate Technologist

*Bureau of Standards*

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APRIL 8, 1922



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### AN IMPROVED METHOD FOR PREPARING RAFFINOSE

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# AN IMPROVED METHOD FOR PREPARING RAFFINOSE

By E. P. Clark

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## ABSTRACT

Owing to the demands made by chemists and bacteriologists for specifications and standards for raffinose, a convenient and economical method for its preparation has been developed so this may be brought about.

Cottonseed meal is extracted with water, the liquor freed from impurities with basic lead acetate, and the raffinose present is removed from the liquid as an insoluble lime compound. This raffinosate is decomposed with  $\text{CO}_2$ , and the free sugar resulting is crystallized from its concentrated sirup by means of alcohol.

A device for carbonating, which is useful for many other purposes, is also described.

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Several methods have been proposed for the preparation of raffinose.<sup>1</sup> All these procedures, however, with the exception of the method of Hudson and Harding, as these authors have well pointed out, have many serious disadvantages. The latter method, while it is a decided improvement over all others and gives fairly good results on very small lots, nevertheless has objectionable features when applied to the preparation of larger quantities of the sugar. Chief among these may be mentioned the tedious procedure in extracting the meal, the necessity of evaporating large quantities of water due to the excessive dilution of the extract, and the quantity and cost of the reagents required. The following method overcomes these disadvantages and enables one to prepare relatively large quantities of this sugar by a convenient and economical process.

Five kilograms of coarsely ground cottonseed meal are thoroughly moistened with 2 liters of water and allowed to stand overnight. The meal is then loosely packed in a cylindrical percolator, and sufficient water added to saturate the meal and leave a stratum above it. When the liquid begins to run from the percolator, more menstruum is added from time to time until a sample of the percolate, after defecation with dry basic lead acetate, has an optical rotation of not more than  $1^\circ$  in a 2 dm tube.<sup>2</sup> The process is then stopped, and the percolate is treated with a solution of basic lead acetate until no more precipitate is formed. The yellow precipitate is filtered off upon large folded filters and finally washed on the filter with a little water. The filtrate and

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<sup>1</sup> E. O. Von Lippmann, *Die chemie der zuckerarten* 3rd ed., p. 1627-1630; 1904. C. S. Hudson and T. S. Harding, *J. Am. Chem. Soc.*, **36**, No. 10, p. 2110; 1914. H. E. Zitkowski, *American Sugar Industry*, **12**, p. 324; 1910.

<sup>2</sup> As there are substances in the meal which are extracted much more slowly than the sugar, and which cause difficulty in the subsequent steps, as well as give an inferior product, it is essential to obtain a quite rapid percolation, consuming not more than 30 to 35 minutes; and it is not expedient to carry the extraction beyond where the optical rotation of the liquid is less than  $1^\circ$  in a 2 dm tube.

washings, which should have a volume of 12 to 13 liters, are freed from the excess of lead with oxalic acid. The lead oxalate is removed and washed on the filter with a little water. The filtrate and washings are thoroughly mixed, measured, and the optical activity of the liquid determined. It is then made distinctly alkaline to litmus with sodium hydroxide. The precipitate thus formed flocks out and settles to the bottom of the vessel in a few minutes. The supernatant liquid is next filtered through a Buchner funnel provided with a thin layer of decolorizing carbon on filter paper. The filtration is rapid under these conditions, and when all has passed through, the precipitate is placed on the filter and drained.

The raffinose is next removed from the solution by forming the insoluble calcium raffinosate. To conveniently accomplish this the liquor is cooled to 10° C or lower, placed in a jar or other suitable container, and rapidly stirred with a mechanical stirring device. As it is being agitated a quantity of powdered active lime, preferably 200 mesh, but not coarser than 100 mesh, sufficient to precipitate all the sugar is slowly sifted in. After all has been added, the stirring is continued for about five minutes. If the lime is active and the optical activity of the solution is calculated to raffinose hydrate with a specific rotation of about 105°, 1 g of lime to 1 g of raffinose is sufficient for complete precipitation. However, unless the activity of the lime is known, it is advisable to test the liquid to see if all the sugar has been removed; if not, more lime should be added. The calcium raffinosate is filtered off, washed by grinding up to a smooth paste with 2½ liters of cold lime water, and again filtered.

It is next carbonated to neutrality. Emphasis is to be laid upon accomplishing this easily and quickly. The device illustrated in Fig. 1 was used for this purpose.<sup>3</sup> The cake of raffinosate is

<sup>3</sup> The design is essentially that developed by C.W. Doherty, of the Great Western Sugar Co., for carbonating beet juices. It consists of an ordinary stirring apparatus that may be clamped to any rigid laboratory support stand. The stirring shaft, *A*, is made of steel tubing 8 mm inside diameter. Just below the shaft support is a union, *B*, to which is joined another section of shafting of the desired length. For most laboratory work a length of 45 cm is sufficient. Attached to the lower end are two triangular plates. These plates, which are 2 mm thick and whose sides are 75 mm long, are held 2 mm apart by 3 rivets near the apex of the angles. The plate attached to the shafting has an opening connecting with the stirring rod. The bottom plate has no opening. *C* is a stuffing box made by simply attaching to the stirring shaft a short piece of good rubber tubing in which is placed a well oiled, closely fitting cork cylinder, *D*, through which a piece of glass tubing, *E*, is inserted. The glass tube is held rigid by means of a clamp, *F*. The cork thus arranged may be made gas tight, and still turn freely, by tightening the rubber tubing about it with a wire. Incidentally, this apparatus may be used to advantage for a number of purposes. In the work described in this paper, where any stirring was done or where precipitates were ground up with water in order to wash them, the stuffing box attachment was removed and the upper orifice of the turning shaft corked. The precipitate was placed in a suitable container with the liquid used to wash it and the apparatus turned for 1 or 2 minutes. At the end of this time the mixture was a perfectly smooth paste, all lumps being completely broken up. It has also been used very effectively in decomposing lead precipitates with hydrogen sulphide. Quantities of lead precipitates which would normally require from 3 to 4 hours for complete decomposition have been decomposed completely in 15 to 20 minutes.

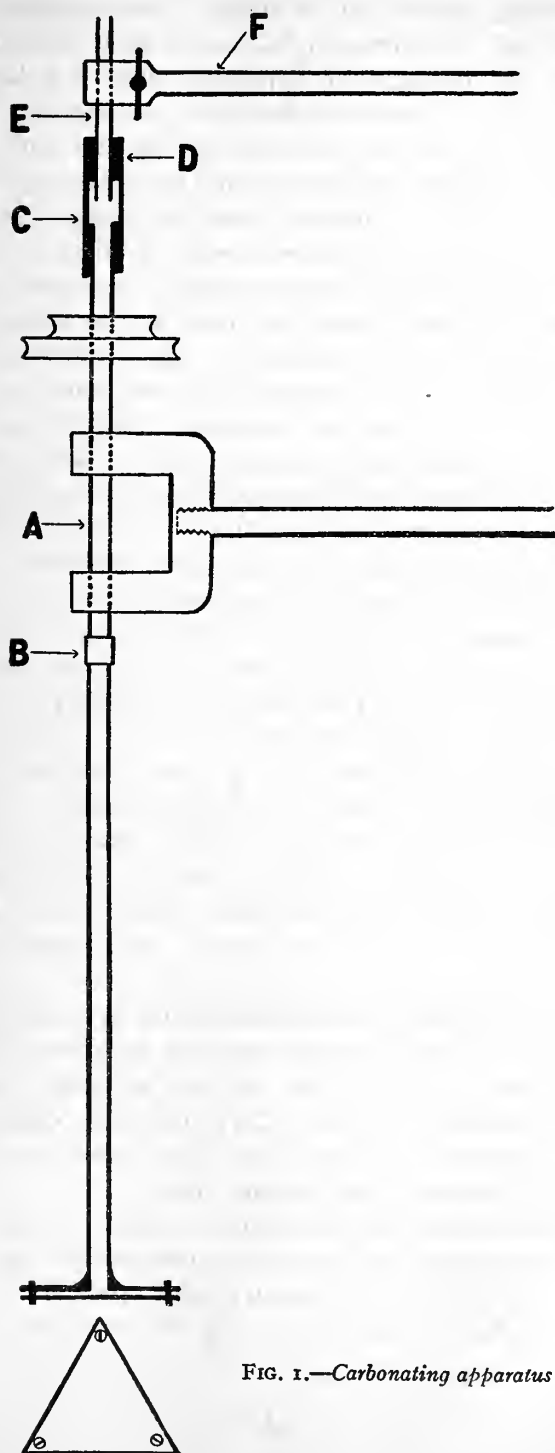


FIG. 1.—Carbonating apparatus

placed in a deep, narrow can of about 8 liters capacity and filled three-fourths full of water at 50° C, and a lively stream of carbon dioxide is passed through the apparatus while it is being turned about 1500 rpm. In this way the gas is centrifugally distributed and neutralizes the lime in 4 or 5 minutes without any loss of CO<sub>2</sub>. The solution is filtered while hot, and the precipitate is washed by grinding up with 2 liters of water and again filtering. The combined liquors are evaporated under diminished pressure to 70 to 75 per cent total solids and warmed to about 60° C. To this sirup 95 per cent ethyl alcohol is added just to saturation. The alcoholic solution is then warmed on the water bath to about 60° C and filtered through a small Buchner funnel in which has been placed a mat of washed asbestos. The filtrate, which is brilliantly clear, is seeded and placed in the ice box to crystallize. Two days are generally sufficient for complete crystallization.

The raffinose is filtered off from the mother liquor, washed first with 80 per cent, then 95 per cent, alcohol, and dried. The yield varies considerably, according to the amount of sugar in the meal; but from a number of different experiments in which different meals were used, yields from 2.3 per cent to 4 per cent were obtained. The crude sugar thus prepared is quite pure, containing only from 0.06 to 0.08 per cent ash.

To purify crude raffinose, a 40 per cent solution (anhydrous sugar) is made by dissolving it in distilled water at 70° C. The warm solution is filtered through a mat of asbestos and placed in the ice box to crystallize. The crystals are freed from mother liquor, washed with 80 per cent, then 95 per cent, alcohol, and dried. A sample of air-dried material thus purified contained 0.005 per cent ash.

An alternative method of recrystallization is to concentrate the above 40 per cent solution under reduced pressure to 70 per cent total solids, warm to 70° C, and add two volumes of 95 per cent alcohol with constant stirring. Crystallization begins almost at once and is complete in a few hours. The crystals are filtered off, washed with 95 per cent alcohol, and dried.

An air-dried sample thus prepared contained 0.015 per cent ash, and its rotation, after being completely dehydrated, was

$$[\alpha]_D^{20} = 123.23 \text{ (10.0136 g per 100.00 cc) ;}$$

$$[\alpha]_{5461}^{20} = 144.95 \text{ (10.0136 g per 100.00 cc)}$$

WASHINGTON, October 7, 1921.



